



Direct Z-scheme g-C₃N₄/WO₃ photocatalyst with atomically defined junction for H₂ production



Weilai Yu^{a,d,*}, Junxiang Chen^a, Tongtong Shang^b, Linfeng Chen^a, Lin Gu^{b,c,**}, Tianyou Peng^a

^a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

^b Beijing National Laboratory for Condensed Matter Physics, Collaborative Innovation Center of Quantum Matter, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

^c School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, China

^d Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

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ABSTRACT

Mimicking the natural photosynthesis, artificial Z-scheme photocatalysis enables more efficient utilization of solar energy for sustainable chemical fuel production. Herein, a direct Z-scheme g-C₃N₄/WO₃ photocatalyst with host-guest architecture is rationally designed, demonstrating significantly enhanced activities of photocatalytic H₂ production. Unprecedented atomic-scale imaging of both the in-plane and interlayer structures in g-C₃N₄ revealed the well-defined interfaces in such architecture, where the 2D g-C₃N₄ layers stand vertically on the flat facets of WO₃ nanocuboids. Through both experimental and theoretical investigations, mechanistic insights regarding the direct Z-scheme electron transfer from WO₃ to g-C₃N₄ were obtained. The Z-scheme electron transfer was driven by the internal electric field at the interfacial junction, defined by the covalent W-O-N-(C)₂ interaction. Under simultaneous light excitation, this atomically defined junction induces a rapid electron injection from WO₃ to inhibit the fast recombination kinetics within g-C₃N₄ and prolong the charge carrier lifetime of g-C₃N₄, thereby liberating more excited electrons with high reducing power for H₂ production.

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1. Introduction

With increasing global energy demand, heterogenous photocatalysis is an effective approach for sustainable solar fuel production [1–3]. Since 1972 when Fujishima and Honda demonstrated the proof-of-concept study by devising a TiO₂/Pt photoelectrochemical cell, the solar-driven H₂ production from water by semiconductor photocatalysts has gained dramatic attention worldwide [4–8]. At present, numerous photoactive semiconductor materials have been discovered for light energy harvesting [9,10]. However, the activity of single-phase semiconductor photocatalyst is greatly limited by its insufficient light absorption and fast recombination of charge carriers. Combining two semiconductors with suitable band alignment is a promising

strategy to yield an enhanced photocatalytic activity, by simultaneously extending light absorption and promoting charge separation [11–14]. Conventional heterojunctions typically result in unfavorable losses of redox ability for photogenerated charge carriers. On the contrary, upon simultaneous two-photon excitation, the dual-band Z-scheme photocatalysts that mimic the natural photosynthesis can maintain both the high reducing and oxidizing power of photogenerated charge carriers and thus elevate the overall utilization efficiency of solar energy [15–19]. Therefore, devising new Z-scheme photocatalytic systems by appropriately interfacing different semiconductor materials is highly desirable.

Graphitic carbon nitride (g-C₃N₄), a stable and nontoxic polymeric semiconductor, was introduced for photocatalytic water splitting under visible-light illumination [20–22]. Due to its narrow band gap (2.7 eV) and negative conduction band (CB) edge position (−1.1 V vs. NHE), g-C₃N₄ is especially suitable to achieve photoinduced reactions of H₂ generation and CO₂ reduction [23–26]. Combining g-C₃N₄ with inorganic semiconductors is a promising strategy to achieve spatial separation of charge carriers and enhanced photocatalytic performances [27–31]. Recently, we showed that the excited electrons in g-C₃N₄ were more likely to

* Corresponding author at: College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China.

** Corresponding author at: Beijing National Laboratory for Condensed Matter Physics, Collaborative Innovation Center of Quantum Matter, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

E-mail addresses: yuweilai93@whu.edu.cn (W. Yu), lg@iphy.ac.cn (L. Gu).

recombine with its holes than interfacially transfer to other coupled inorganic semiconductors [29]. Thus, a full exploitation of the excited electrons in g-C₃N₄ with high reducing power highly necessitates the fabrication of Z-scheme photocatalytic systems.

To realize this goal, a host-guest concept is rationally employed here by embedding the guest WO₃ nanocuboids in the host g-C₃N₄ polymers to achieve materials integration with intimate interfacial contact [32–34]. The more positive band edges and the higher electron mobility of metal oxides are expected to concurrently enable a rapid electron injection into the valence band (VB) of g-C₃N₄ under type-II band alignment, thereby greatly retarding the fast recombination kinetics of g-C₃N₄ and promoting the photocatalytic performances. Although there are several previous reports on the enhanced photocatalytic performances of the g-C₃N₄/WO₃ composites, the underlying physical and structural factors responsible for the interfacial charge transfer have not been clearly identified [35–38]. Thus, it is clear that a combined study of experimental and theoretical investigations is highly necessary to provide deeper mechanistic insights towards more comprehensive understanding of this binary system. Moreover, similar band gaps of g-C₃N₄ and WO₃ also make g-C₃N₄/WO₃ an almost ideal system to evaluate the charge separation efficiency and interfacial junction performances by maintaining nearly the same light absorption range and charge carrier generation rate.

In this work, we design such a host-guest architecture *via* partial intercalation of the WO₃ nanocuboids (guest) within g-C₃N₄ (host) featuring their simultaneous exposure to light illumination. Despite the inactivity of WO₃ for direct photocatalytic H₂ production, the resulting g-C₃N₄/WO₃ composites all exhibited significantly enhanced photoactivities, compared with pure g-C₃N₄. With the aid of spherical aberration-corrected scanning transmission electron microscopy (STEM), the well-defined interfaces between g-C₃N₄ and WO₃ were clearly resolved. Unprecedentedly, both the in-plane and interlayer structures of g-C₃N₄ were directly imaged at atomic scale. Combined with investigations of the interfacial charge density migration and charge carrier effective masses, it is revealed that this significant enhancement of photocatalytic activity benefits from the direct Z-scheme electron transfer from WO₃ into g-C₃N₄, driven by their internal electric field at the atomically defined junction. The rapid electron injection from WO₃ into g-C₃N₄ results in both slower recombination rate and prolonged lifetime of photogenerated charge carriers in the bulk g-C₃N₄. In this way, this Z-scheme host-guest architectural design enables more efficient utilization of the excited electrons in g-C₃N₄ with high reducing power for photocatalytic H₂ generation.

2. Experimental

2.1. Material synthesis

All chemicals were of analytical grade and used without further purification.

2.1.1. Synthesis of WO₃ nanocuboids

Sodium tungstate dihydrate (Na₂WO₄·2H₂O) is used as the precursor of monoclinic WO₃ nanocuboids and lactic acid is adopted as the capping agent to control its size and morphology [39]. In a typical synthesis, 1.0 g sodium tungstate dihydrate was first dissolved in 50 mL deionized water under vigorous stirring for 15 min. Then 1 mL lactic acid was added dropwise into the above solution and then the original colorless transparent solution gradually turned into light yellow. After continuous stirring for another 15 min, the pH of the solution was adjusted to 1.0 by adding 3 M HCl solution dropwise. Then the solution gradually turned into yellow gel type mixture and an additional 20 min stirring was given to ensure the

homogeneity of the solution. The resulting mixture was then transferred to a 80 mL Teflon-lined stainless steel autoclave. After the autoclave was tightly sealed, it was put into the oven for reaction at 180 °C for 24 h. A blue suspension was obtained afterwards and water and ethanol were used alternatively to remove the residues in the obtained products. The final products were collected by intense centrifugation and turned into yellow after drying in oven at 80 °C overnight. The XRD results confirmed that the final products were monoclinic WO₃ formed by the hydrolysis of tungstate anions under acidic environment.

2.1.2. Synthesis of host/guest g-C₃N₄/WO₃ nano-architecture

2.40 g of melamine and a specific amount (*x* mg) of the as-prepared WO₃ nanocuboids were put into a crucible. The above solids were uniformly mixed in 20 mL ethanol and dispersed to form a suspension under vigorous stirring for 30 min. Then the crucible was put in the oven at 80 °C to remove the ethanol. Due to the low surface tension of ethanol, a light yellow solid mixture with smooth surface was then deposited at the bottom of crucible. Afterwards, the crucible was put into muffle furnace and was heated to 550 °C for 2 h with a heating-up time of 1 h. When cooled to room temperature, the obtained solid was ground to fine powder. Because of the same amount of melamine used in the syntheses of various samples, the resulting g-C₃N₄/WO₃ composites were labelled as GW*x*, where *x* indicated that *x* mg of the WO₃ nanocuboid was mixed with melamine. For the purpose of comparison, both pure g-C₃N₄ and WO₃ were also prepared *via* the same synthetic route.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a D/Max-RB X-ray diffractometer (Rigaku, Japan) under Cu K α radiation at a scan rate (2 θ) of 0.05° s⁻¹. The accelerating voltage and applied current were 40 kV and 80 mA, respectively. Thermogravimetric analysis (TGA) of all samples was performed on a DTG-60H analyzer (Shimadzu Corp., Tokyo, Japan) to investigate their thermal properties. The temperature was heated from ambient to 900 °C at a rate of 10 °C min⁻¹, using around 5 mg of each sample. UV–vis absorbance spectra were obtained on a UV–vis spectrophotometer (UV-2550, SHIMADZU, Japan) using die-pressed disk samples, in which BaSO₄ was used as the reflectance standard. Fourier transform infrared (FT-IR) spectra of the samples were recorded on an IR Affinity-1 FT-IR spectrometer, using conventional KBr pellets in the range of 4000–500 cm⁻¹ at room temperature. The solid-state NMR experiments were carried out at 11.7 T on a Bruker-500 spectrometer using the ¹H → ¹³C CP/MAS NMR technique with the MAS spinning speed of 10 kHz, equipped with a double-resonance 4 mm probe. The $\pi/2$ pulse length for ¹H was 4.1 μ s, the contact time was 5.5 ms, and the repetition time is 7.0 s. The chemical shifts were referenced HMB for ¹³C. Field-emission scanning electron microscopy (FE-SEM) images and energy-dispersive X-ray (EDX) mapping profiles were obtained on a JSM-7500F scanning electron microscope (JEOL, Japan). Transmission electron microscopy (TEM) analyses were conducted on a Tecnai G² F20 S-TWIN microscope at an accelerating voltage of 200 kV. Spherical aberration-corrected scanning transmission electron microscopy (STEM) images were obtained using an ARM-200CF (JEOL, Japan) transmission electron microscope operating at 200 kV equipped with double spherical aberration (Cs) correctors. Nitrogen adsorption–desorption isotherms were measured on an ASAP 2020 nitrogen adsorption apparatus (Micromeritics, USA). All samples were degassed at 180 °C before measurements. The BET surface areas were determined by a multipoint BET method using the adsorption data in the relative pressure (P/P₀) range of 0.05–0.25. The pore size distributions were determined using des-

orption data by the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) measurements were obtained on an ultrahigh-vacuum VG ESCALAB 210 electron spectrometer equipped with a multi-channel detector. The spectrum was excited by Mg K α radiation of two anodes in the constant analyzer energy mode at 200 W. All the binding energies were referenced to the C 1s peak at 285.0 eV of the surface adventitious carbon. Photoluminescence (PL) emission spectra were measured on an F-7000 Fluorescence Spectrophotometer (Hitachi, Japan) at room temperature. The excitation wavelength is 315 nm, the scanning speed is 1200 nm min⁻¹ and the photomultiplier tube (PMT) voltage is 700 V. The width of both the excitation slit and the emission slit were 2.5 nm. Time-resolved transient photoluminescence decay profiles were obtained on a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK). The time-dependent fluorescence curves were fitted through the bi-exponential model to calculate the shorter (τ_1) and longer (τ_2) lifetime [40,41].

2.3. Photocatalytic activity test

Photocatalytic H₂-production reactions were performed in a 100 mL three-neck Pyrex flask at room temperature, with three openings of the flask sealed with rubber plugs. In a typical activity test, 50 mg of photocatalyst powder was uniformly suspended by ultra-sonication in 80 mL of aqueous solution containing 10 vol.% triethanolamine (TEOA) as sacrificial reagent. In order to photochemically deposit Pt co-catalyst onto the photocatalyst surface, 0.1 mL of H₂PtCl₆·6H₂O aqueous solution (1 g/100 mL) was added into the suspension and the system was then exposed to a 300 W Xe arc lamp (Changzhou Siyu Science Co. Ltd., China) for 30 min of light irradiation. The reactant suspension was then bubbled with nitrogen gas for 30 min to ensure anaerobic environment. Next, 1 h of simulated solar irradiation was performed using the same 300 W Xe arc lamp under continuous stirring. 0.4 mL of gas was sampled by a microsyringe and the evolved hydrogen was evaluated by a gas chromatograph (GC-14C, Shimadzu, Japan) equipped with thermal conductive detector, 5 Å molecular sieve column and pure nitrogen as carrier gas. Cycled tests of photocatalytic H₂ production were performed by continuous sampling the gas products every one hour and re-bubbling the suspension with nitrogen gas for 30 min every three hours, without changing the original solutions of sacrificial reagents.

2.4. Photoelectrochemical measurements

Photoelectrochemical measurements were performed on a CHI 660D electrochemical workstation (Chenhua Instrument, Shanghai, China) in a conventional three-electrode configuration. The working electrode prepared with the sample has an active area of ca. 1 cm². A Pt wire and a Ag/AgCl electrode were used as the counter and reference electrode, respectively. A low-power LED (3 W, 365 nm, Shenzhen LAMPLIC Science Co. Ltd. China) with an intensity of ca. 80.0 mW cm⁻² was used as the light source. 0.5 M Na₂SO₄ aqueous solution was used as the electrolyte. Typically, the working electrodes were prepared as follows: 0.2 g of photocatalyst powder was mixed with 0.08 g of polyethylene glycol (molecular weight: 20,000) and 2 mL of ethanol. Then, the mixture was ground to form a slurry and the slurry was coated onto a pre-cleaned 2 cm × 1.2 cm F-doped SnO₂-coated glass (FTO glass) electrode via a doctor blade technique. After drying, the prepared electrodes were calcined at 450 °C for 30 min in a muffle furnace, with a heating rate of 5 °C min⁻¹.

2.5. DFT calculation

2.5.1. Population analysis of g-C₃N₄/WO₃ interface

The g-C₃N₄/WO₃ interface was constructed by placing (C₃N₄)_n above the WO₃ (200) surface based on the proposed chemical bonding pattern in Fig. 3i. Spin-polarized DFT calculations were performed with periodic super-cells under the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) functional for exchange–correlation and the ultrasoft pseudopotentials for nuclei and core electrons. The Kohn–Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cutoff of 30 Ry and the charge-density cutoff of 300 Ry. The Fermi-surface effects have been treated by the smearing technique of Methfessel and Paxton, using a smearing parameter of 0.02 Ry. Periodically repeated four-layer slabs structure were used to model the WO₃ (100) surface. The bottom two layers fixed to DFT-optimized equilibrium lattice constant of 14.7626 Å. The top two layers were allowed to relax with the adsorbates during the calculations until the Cartesian force components acting on each atom were below 10⁻³ Ry/Bohr and the total energy converged to within 10⁻⁵ Ry. A Slab of (2 × 2) is used and the Brillouin zones were sampled with a 4 × 4 × 1 k-point mesh. The PWSCF codes contained in the Quantum ESPRESSO distribution were used to implement most of the calculations [42].

2.5.2. Calculation of charge carrier effective mass

The charge carrier effective masses of g-C₃N₄ and WO₃ were investigated using first-principle DFT calculations based on a CASTEP code and the plane-wave pseudopotential method. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) was used as the exchange–correlation function. The interaction between the ionic core and valence electrons was described by The ultrasoft pseudopotential. The lattice parameters and atomic coordinates were relaxed using a cutoff energy of 380 eV and Monkhorst-pack grids of 4 × 4 × 2 k-points for both g-C₃N₄ and WO₃ models. Geometric optimization was first achieved using convergence thresholds of 2 × 10⁻⁵ eV per atom for total energy, 0.03 eV Å⁻¹ for maximum force, 0.05 GPa for pressure, and 0.001 Å for maximum displacement. The self-consistent calculations were performed with a total tolerance of less than 1 × 10⁻⁶ eV per atom. After geometric optimizations, the effective masses of charge carriers were calculated based on the obtained electronic band structures.

The charge carrier effective mass was calculated by parabolic fitting to the conduction band minimum (CBM) and valence band maximum (VBM) based on Eq. (1). Basically, the effective mass of a charge carrier is inversely proportional to its moving velocity according to Eq. (2), where ν and m^* represent the transfer rate and effective mass of a charge carrier, respectively. Thus, a smaller value of charge carrier effective mass (m) corresponds to a faster transfer rate.

$$m^* = \hbar^2(d^2E/dk^2)^{-1} \quad (1)$$

$$\nu = \hbar k/m^* \quad (2)$$

To evaluate the charge separation efficiency, the concept of relative effective mass (R) was adopted based on Eq. (3). In general, a higher value of R means the higher separation tendency of photo-generated electron–hole pairs, resulting in slower recombination rate and better photocatalytic performance.

$$R = m_h^*/m_e^* \quad (3)$$

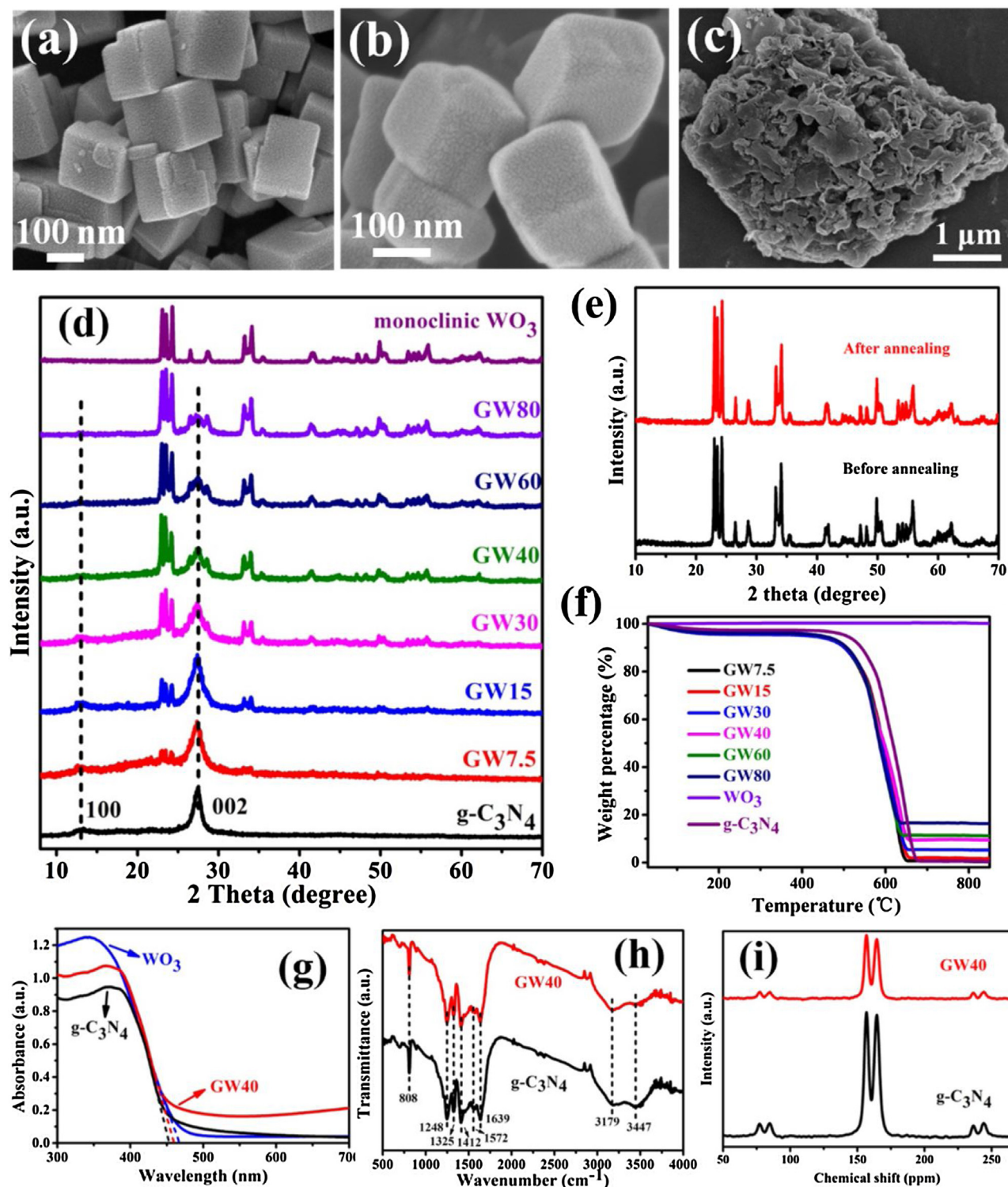


Fig. 1. (a–c) FE-SEM images of pristine WO_3 nanocuboids (a) before and (b) after annealing and (c) pure $\text{g-C}_3\text{N}_4$; (d) XRD patterns for all the samples; (e) comparison of XRD patterns of pristine WO_3 before and after annealing; (f) TGA curves for all the samples; (g) UV-vis diffuse reflectance spectra (DRS) of pure $\text{g-C}_3\text{N}_4$, WO_3 and GW40; (h) FT-IR spectra of and (i) ^{13}C CP-MAS NMR spectra of pure $\text{g-C}_3\text{N}_4$ and GW40 composite.

3. Results and discussions

Firstly, WO_3 nanocuboids were prepared via hydrothermal hydrolysis of tungstate anions using lactic acid as capping agent. These nanocuboids exhibited uniform sizes with length of 150–200 nm and generally exposed flat and smooth crystal facets with sharp edges as shown in Fig. 1a. The morphol-

ogy of WO_3 nanocuboids was largely maintained after annealing (Fig. 1b). Their edges grew smoother due to the surface roughening effect. Pure $\text{g-C}_3\text{N}_4$ condensed from melamine showed large and compact microstructures whose extended length reached $5\text{ }\mu\text{m}$ in Fig. 1c. Each individual microstructure was aggregated from densely packed lamellar structures demonstrating polymeric flexibility. The $\text{g-C}_3\text{N}_4/\text{WO}_3$ composites were fabricated via thermal

Table 1
Weight content of WO₃ in different GWx composites.

Sample	WO ₃ weight percentage/%
GW7.5	0.7
GW15	2
GW30	5.4
GW40	9.6
GW60	11.5
GW80	16.6

annealing of homogeneously mixed solids of melamine and the as-prepared WO₃ nanocuboids. The resulting composites were labelled as GWx according to the weight content of WO₃. The X-ray diffraction (XRD) patterns shown in Fig. 1d reveal that the pristine WO₃ appears as the monoclinic phase. Moreover, the WO₃ nanocuboids feature the exposed (200), (020) and (002) crystal facets with high and similar diffraction intensities [39]. No significant change of crystal phase was observed for pristine WO₃ before and after annealing (Fig. 1e). The relative diffraction intensity of WO₃ gradually increased with increasing ratio of WO₃ in the composites. TGA analysis in Fig. 1f reveals a comparable thermal stability of GWx composites as that of pure g-C₃N₄. More than 80% of the weight content in all the prepared GWx samples refers to the bulk g-C₃N₄ phase (Table 1). In this regard, g-C₃N₄ in GWx acts as a bulk host material residing the guest WO₃ nanocuboids. The absorption edges of g-C₃N₄ and WO₃ were measured to be 450 and 470 nm by UV–vis DRS (Fig. 1g), corresponding to their intrinsic band gaps of 2.7 eV and 2.6 eV, respectively. This shows that g-C₃N₄ and WO₃ has similar band gaps and nearly the same range of light absorption. The increased light absorption of GW40 sample at wavelength larger than 450 nm may be attributed to the defect states in g-C₃N₄ due to the incorporation of WO₃ nanocuboids during its polymerization [24]. Furthermore, the chemical structure of g-C₃N₄ in GW40 was proved to be the same as that of pure g-C₃N₄ by both FT-IR spectra (Fig. 1h) and solid-state ¹³C NMR spectra (Fig. 1i). In the FT-IR spectra, the peaks at 1248, 1325 and 1412 cm^{−1} are assigned to the aromatic C–N stretching, while the peaks at 1572 and 1639 cm^{−1} are attributed to the C–N stretching vibration modes. The peaks at 808 cm^{−1} belong to the out of plane bending modes of triazine units, indicating the presence of condensed C–N heterocycles. Moreover, the broad absorption bands at 3179 and 3447 cm^{−1} are due to the adsorbed H₂O molecules and the N–H vibrations of the uncondensed amine groups [29]. For the solid-state ¹³C NMR measurements, the strong peaks at 156.8 and 164.5 ppm for both GW40 and pure g-C₃N₄ represent the C atoms in the melem (CN₃) and the C atoms connected to the tertiary N atoms within the tri-s-triazine units, respectively [43].

Fig. 2a–e demonstrates the typical morphology of GW40 consisting of 9.6 wt.% WO₃. As seen in Fig. 2a, its bulk g-C₃N₄ phase exhibited similar densely packed morphology as pure g-C₃N₄. The corresponding EDX mapping profiles revealed that the WO₃ nanocuboids were dispersedly intercalated within the bulk g-C₃N₄. The enlarged view in Fig. 2b showed that the WO₃ nanocuboids were actually partially wrapped within the g-C₃N₄ microstructure. The distinct crystal edges of WO₃ nanocuboids could be clearly identified, with flexible g-C₃N₄ polymer attached onto their flat facets. Consistently, the TEM images in Fig. 2c, d confirmed that disperse distribution of WO₃ nanocuboids within g-C₃N₄, forming an intimate interfacial contact. Structurally, the disperse existence and partial intercalation of WO₃ nanostructures in the bulk g-C₃N₄ can not only benefit their interfacial charge transfer but also maintain their simultaneous exposure to light illumination. Moreover, the HRTEM image and the SAED pattern reveal the single-crystalline nature of WO₃ nanocuboids, ensuring its effective charge carrier transport at nanoscale towards the g-C₃N₄/WO₃ interface (Fig. 2e, f) [44]. As denoted by dashed lines in Fig. 2c, some incompact grain

Table 2
Specific surface area, pore volume and pore diameter of pristine WO₃, GW40 and g-C₃N₄.

Sample	S _{BET} /m ² g ^{−1}	V _{pore} /cm ³ g ^{−1}	d _{pore} /nm
WO ₃	3.3	0.01	10
GW40	34	0.16	19.2
g-C ₃ N ₄	23	0.11	19.1

boundaries were also found in bulk g-C₃N₄ according to the positions of intercalated WO₃ nanocuboids. It can be estimated that the condensation of g-C₃N₄ occurred based on the presence of WO₃ nanocuboids and these imperfect areas suggest that the g-C₃N₄ polymer could physically confluence during their extension from different WO₃ nanocrystals. Compared with pure g-C₃N₄, the increased BET surface area and pore sizes of the GW40 sample are also consistent with these observed imperfect and less compact regions within the g-C₃N₄/WO₃ composite (Fig. 2g and Table 2).

To obtain insights into the structure of g-C₃N₄/WO₃ interface, spherical aberration-corrected scanning transmission electron microscope (AC-STEM) images of GW40 are shown in Fig. 3a, b. For the first time, both the in-plane and interlayer structure of g-C₃N₄ were directly imaged at atomic scale. Fig. 3a reveals the annular bright field (ABF) imaging of the (100) in-plane structure of g-C₃N₄ (top) connected with the WO₃ lattice. The four-coordinated matrix at bottom is assigned to the (002) plane of monoclinic WO₃, where each dark spot refers to one heavy W atom inter-connected by lattice O atoms. Interestingly, the g-C₃N₄ phase demonstrates as an assembly of regularly arranged triangular units with the same spatial orientation. Each of these triangular units is composed of three individual dark spots. Considering the extended network of tri-s-triazine units of g-C₃N₄, each triangular unit actually represents a tri-s-triazine unit (C₆N₇), while each individual dark spot corresponds to a six-membered ring of triazine heterocycle (C₃N₃). Owing to the electron delocalization in π - π conjugated aromatic system, each C₃N₃ triazine ring acts as one basic repeating unit with relatively large atomic number and reflects the in-plane periodicity of the g-C₃N₄ crystal structure under STEM imaging. Similar phenomena were observed in other delocalized π - π conjugated systems including graphene and carbon-doped boron nitride [45,46]. The tertiary nitrogen atoms cross-linking tri-s-triazine building blocks are not observed due to their very small atomic number. The same orientation of all triangular units gives a strong proof that the structure of g-C₃N₄ should be assigned to the regularly extended tri-s-triazine network rather than a layered structure oppositely connected by linear melon chains [20,47]. Besides, each triangular unit was surrounded by six others, which was consistent with the spatial distribution of tri-s-triazine units in the extended network of g-C₃N₄. The inter-space between two neighboring triangular units was measured to be around 0.68 nm by Fast Fourier transform (FFT) analysis. This agreed well with the theoretical distance of (100) plane of g-C₃N₄, corresponding to the periodic distance between two adjacent tri-s-triazine units. More careful observation of the interfacial area between g-C₃N₄ and WO₃ shows that the triangular units of g-C₃N₄ at the interface are unbroken, revealing the existence of complete tri-s-triazine units. More importantly, these tri-s-triazine units are well aligned with the lattice fringes of (200) plane of WO₃ (solid lines). This perfect lattice alignment indicates the existence of well-defined W–O–N(C)₂ covalent bonds at interface. Fig. 3b exhibits the interlayer stacking of 2D planar structures of g-C₃N₄ standing on the flat surface of WO₃ nanocuboids under high angle annular dark-field (HAADF) imaging. The ABA periodic stacking pattern along the [002] crystal axis of g-C₃N₄ could be clearly distinguished. Besides, the [002] crystal axis of g-C₃N₄ is parallel to the WO₃ surface, suggesting the vertical alignment of 2D layered g-C₃N₄ on the flat facet of WO₃

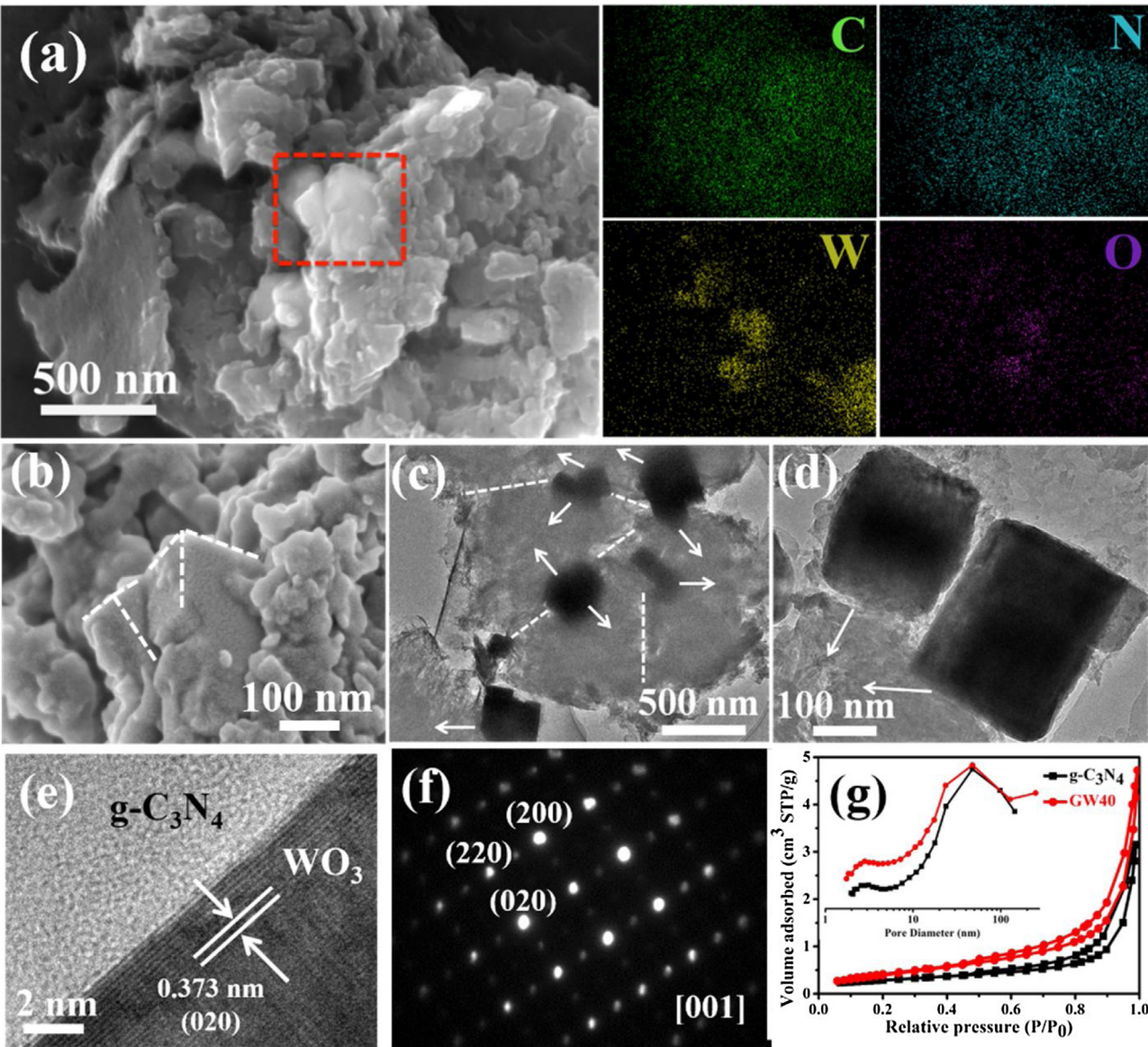
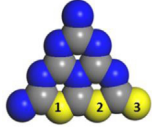
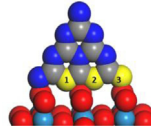
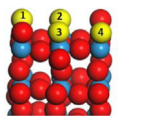
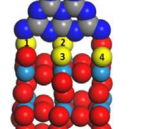


Fig. 2. (a) FE-SEM image of GW40 composite and its corresponding EDX mapping profiles; (b) an enlarged view of the selected area in (a) and the white dashed lines represent the identified WO_3 crystal edges; (c, d) TEM images of GW40 composite; the white dashed lines and the arrows represent the incompact regions in bulk $\text{g-C}_3\text{N}_4$ and its possible extension directions based on WO_3 nanocuboids, respectively; (e) HR-TEM image of crystal lattice fringes of the (020) plane of WO_3 nanocuboid with a distance of 0.373 nm and (f) its corresponding selected area electron diffraction (SAED) pattern; (g) nitrogen adsorption-desorption isotherms and pore size distributions (inset) of pure $\text{g-C}_3\text{N}_4$ and GW40.

Table 3
Calculated charge values of the N atoms in $\text{g-C}_3\text{N}_4$ and the O atoms in WO_3 before and after their interfacing. The gray, dark blue, red and light blue balls represent C, N, O, W atoms. The denoted N and O atoms are labelled with both yellow color and number.

Strucutres				
Atom number	$\text{g-C}_3\text{N}_4$	$\text{g-C}_3\text{N}_4@\text{WO}_3$	WO_3	$\text{WO}_3@\text{g-C}_3\text{N}_4$
1	5.25	5.20	6.15	6.18
2	5.26	5.20	6.16	6.17
3	5.17	5.11	6.16	6.18
4	–	–	6.16	6.19

nanocuboids. In this regard, the flat facets of WO_3 nanocuboids are critical platforms to realize the direct atomic-scale imaging of $\text{g-C}_3\text{N}_4$ structures.

To reveal the electron density migration at the $\text{g-C}_3\text{N}_4/\text{WO}_3$ interface, high-resolution XPS spectra were obtained to elucidate the surface chemical states. Significant binding energy shifts are

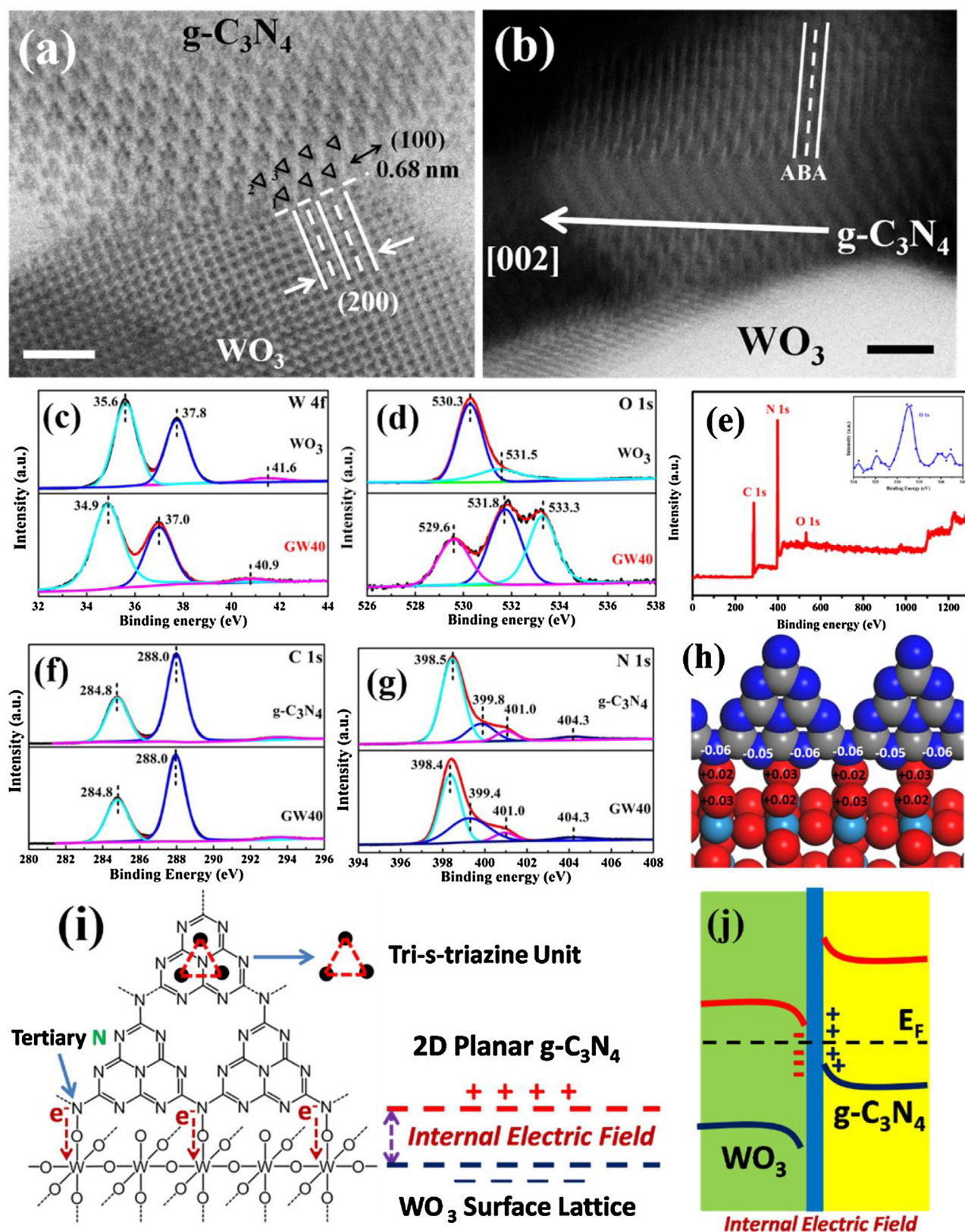


Fig. 3. (a, b) Spherical aberration-corrected STEM images of the well-defined interface between g-C₃N₄ and WO₃ nanocuboids in GW40 composite, revealing both the (a) in-plane and (b) interlayer structure of g-C₃N₄ (scale bars, 2 nm); (c, d) high-resolution XPS spectra of (c) W 4f and (d) O 1s; (e) XPS survey spectrum of pure g-C₃N₄ and inset of its binding energy peak of O 1s state located at ca. 532–533 eV; (f, g) high-resolution XPS spectra of (f) C 1s and (g) N 1s; (h) the optimized structure of the g-C₃N₄/WO₃ interface with the change of electron density distribution, obtained by Lowdin charge analysis; the gray, dark blue, red and light blue balls represent the C, N, O and W atoms, respectively; the associated signed values (unit: e⁻) show that after structure optimization, the interfacial N and O atoms lose and gain electrons, respectively; (i) schematic illustration of the atomically defined junction at the g-C₃N₄/WO₃ interface and the internal electric field from g-C₃N₄ (+) to WO₃ (-); (j) energy band diagram between WO₃ and g-C₃N₄ with inverse band bending and internal electric field at interface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

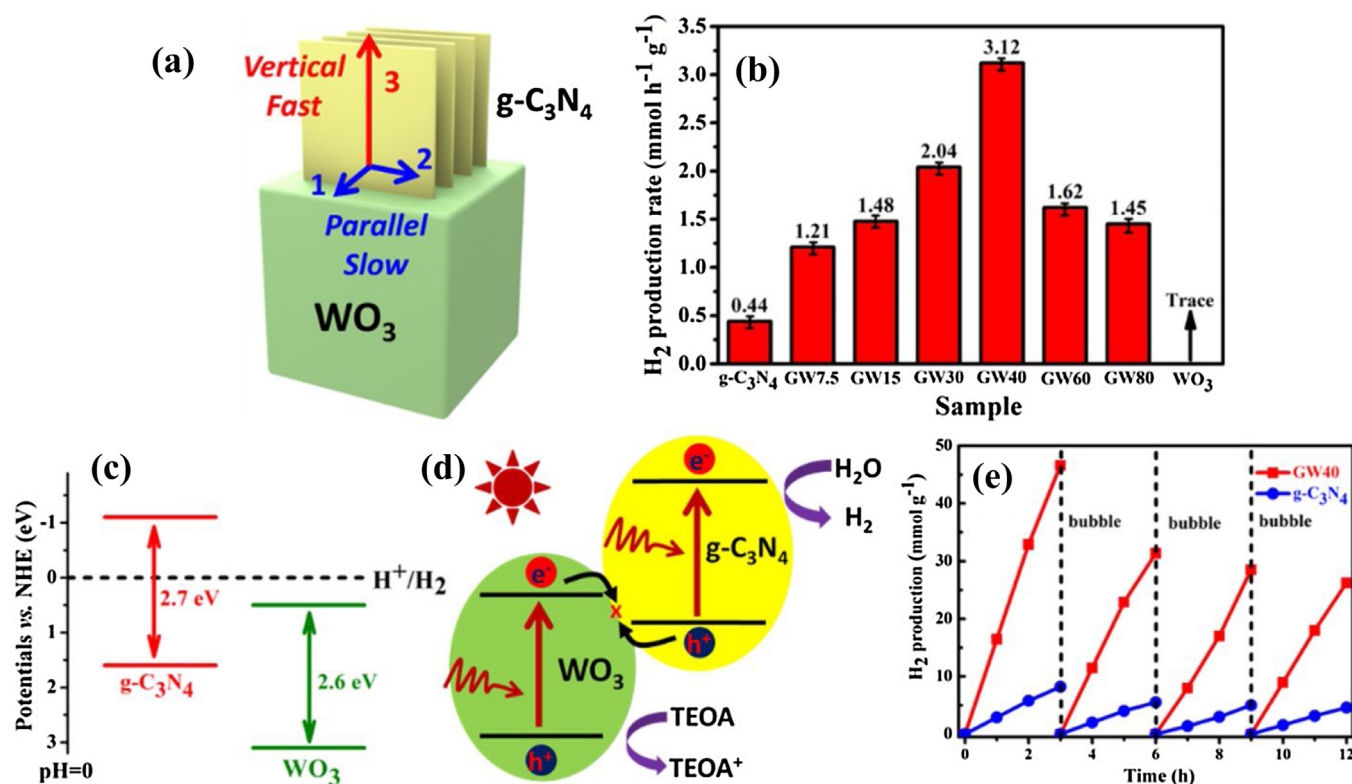


Fig. 4. (a) Schematic diagram of the growth and extension of g-C₃N₄ in parallel (1 and 2, slow) and vertical (3, fast) direction to the flat surface of WO₃ nanocuboids; (b) Comparison of average photocatalytic H₂ production rates of GWx composites and pure samples loaded with 1 wt.% Pt co-catalyst for the first three hours under simulated solar irradiation; (c) band energy diagram of the type-II band alignment between g-C₃N₄ and WO₃ in GWx composites, in comparison to the NHE; (d) schematic diagram of the direct Z-scheme electron transfer from WO₃ to g-C₃N₄; (e) comparison of the cycled tests of photocatalytic H₂ production for the GW40 sample and pure g-C₃N₄.

evident for both W 4f and O 1s states. The W 4f spectrum of pristine WO₃ in Fig. 3c demonstrates two major peaks at 35.6 (W 4f_{7/2}) and 37.8 eV (W 4f_{5/2}), which can be assigned to the W⁶⁺ ions of WO₆ octahedral in monoclinic WO₃. In contrast to pristine WO₃, all peaks of W states in GW40 are consistently shifted towards lower energy by 0.7–0.8 eV, indicating a decrease in the W oxidation state. The O 1s spectrum of pristine WO₃ in Fig. 3d exhibits two peaks at 530.3 and 531.5 eV. The strong main peak at 530.3 eV can be attributed to the lattice O atoms of WO₃, while the weak shoulder peak at 531.5 eV can be assigned to the terminal hydroxyl groups (–OH) on surface. Three independent peaks at 529.6, 531.8 and 533.3 eV are found for the O 1s state of GW40. The peaks at 531.8 and 533.3 eV are assigned to the oxygen atoms in g-C₃N₄, due to the oxidation effect during thermal condensation. This is consistent with the O 1s state found in the XPS survey spectrum (Fig. 3e) of pure g-C₃N₄ at ca. 532–533 eV and the large oxygen-to-tungsten ratio (10.5) of GW40. Thus, only the peak at 529.6 eV is ascribed to the WO₃ phase, which is also shifted to lower energy by 0.7 eV as compared with pristine WO₃. In this regard, the significant decrease of binding energy for both W and O elements suggests that the total electron density increased in the WO₃ phase of GW40 and this redundant electron density is shifted from g-C₃N₄. However, the C 1s and N 1s spectra of GW40 show negligible differences from those of pure g-C₃N₄ (Fig. 3f, g). The absence of considerable binding energy shift for both C and N elements can be attributed to the large weight content and the giant sizes of g-C₃N₄ in GW40. Also, the ratio of its surface atoms in contact with WO₃ nanocuboid can also be considered much smaller, compared with the much larger ratio of surface atoms for the nano-sized WO₃ crystals. Thus, it is clear that the significant decrease of binding energy in WO₃ indicated the electron density migration from g-C₃N₄ to WO₃.

Based on the above STEM images, the chemical bonding pattern of the well-defined g-C₃N₄/WO₃ interface was proposed in Fig. 3h, i. Each tertiary N atom linking two tri-s-triazine units of g-C₃N₄ form covalent bonds with one dangling W–O bond on WO₃ surface lattice. The flexibility of the surface dangling W–O bonds could compensate for the slight mismatch between the (100) plane of g-C₃N₄ and the surface lattice of WO₃. Such interfacial covalent interaction forms an atomically defined junction and paves a direct pathway for electron transfer, thus greatly facilitating the spatial separation of charge carriers. Based on this proposed structure, theoretical DFT calculations of charge distribution at the structurally optimized g-C₃N₄/WO₃ interface were also performed. Consistent with the XPS spectra, the calculated results confirm the existence of the electron density shift from g-C₃N₄ to WO₃ at ground state (Fig. 3h and Table 3). According to the energy band alignment between g-C₃N₄ and WO₃, this migration of electron density is possible due to the different Fermi energy levels of g-C₃N₄ (higher) and WO₃ (lower). The equilibration of their different Fermi energy levels produces an internal electric field from g-C₃N₄ (+) to WO₃ (–) (Fig. 3i) and further drives the energy bands of g-C₃N₄ and WO₃ phase to bend up and down at their interface, respectively (Fig. 3j) [48]. Under simultaneous light excitation, the opposite band bending is expected to promote the recombination between the electrons in the CB of WO₃ and the holes in the VB of g-C₃N₄, thus driving the direct Z-scheme charge transfer without the aid of any electron transfer mediator.

The presence of this well-defined interface again indicates that the condensation of melamine to form polymeric g-C₃N₄ takes place in a modulated manner over the flat surface of WO₃ nanocuboids. The dangling W–O bonds can serve as the active sites and first form covalent bonds with the tertiary N atoms of

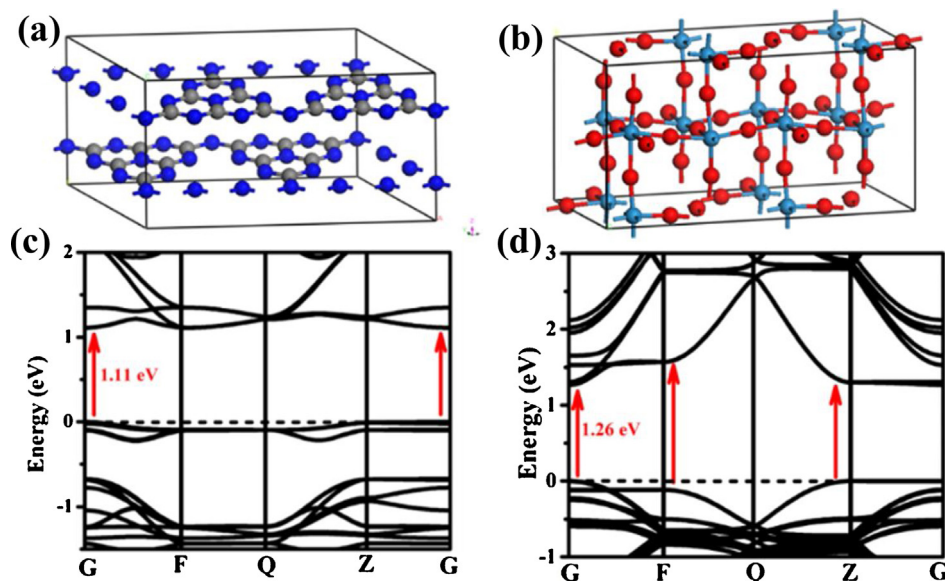


Fig. 5. (a, b) Crystals structures of (a) $g\text{-C}_3\text{N}_4$ and (b) monoclinic WO_3 ; the dark blue, gray, light blue and red balls represent N, C, W and O atoms, respectively; (c-d) the calculated electronic band structures of (c) $g\text{-C}_3\text{N}_4$ and (d) WO_3 based on the above crystal structures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

melamine. After initial polymerization of melamine, $g\text{-C}_3\text{N}_4$ could further grow in three different directions: (a) interlayer stacking and (b) in-plane extension by aligning with the WO_3 surface lattice and (c) unlimited vertical growth (Fig. 4a). Due to the regulations of simultaneous WO_3 surface roughening and the required molecular conformation, both the parallel stacking and extension of $g\text{-C}_3\text{N}_4$ along the interface are expected to occur in a much slower rate than its unlimited vertical growth. In this way, these vertically aligned 2D $g\text{-C}_3\text{N}_4$ layers could undergo fast perpendicular growth and then self-organize into densely packed large microstructures. As a result, small WO_3 nanocuboids were dispersedly embedded as guest within the surface regions of the host $g\text{-C}_3\text{N}_4$ microparticles. Also, the physical confluence of $g\text{-C}_3\text{N}_4$ grown from different WO_3 nanocuboids formed many incompact areas observed in Fig. 2c. Owing to the different rates in parallel and vertical extension, the WO_3 surface was only partly wrapped in $g\text{-C}_3\text{N}_4$, which is beneficial to achieve their simultaneous light excitation.

The photocatalytic H_2 -production activity of samples was evaluated in 10 vol% TEOA aqueous solution under simulated solar irradiation. A comparison of the average photocatalytic H_2 production rates is shown in Fig. 4b. After loading 1 wt.% Pt co-catalyst, pure $g\text{-C}_3\text{N}_4$ only exhibited a moderate rate of photocatalytic H_2 production ($0.44 \text{ mmol h}^{-1} \text{ g}^{-1}$). Pristine WO_3 nanocuboids failed to show any appreciable photocatalytic H_2 -production activity. This was due to its more positive CB edge position (ca. 0.3 V vs. NHE) than the standard potential of H^+/H_2 redox couple (Fig. 4c) [49]. Thus, only the excited electrons from the CB of $g\text{-C}_3\text{N}_4$ (ca. -1.1 V vs. NHE) have enough reducing power for the H_2 production reaction. However, when embedding a small amount of inactive WO_3 nanocuboids into $g\text{-C}_3\text{N}_4$, all the fabricated GWx composites exhibited significantly enhanced activities in contrast to pure $g\text{-C}_3\text{N}_4$. Especially, GW40 exhibited the highest H_2 production rate ($3.12 \text{ mmol h}^{-1} \text{ g}^{-1}$), which is 7 times higher than that of pure $g\text{-C}_3\text{N}_4$. By comparing the band edge positions of $g\text{-C}_3\text{N}_4$ and WO_3 , the dramatic enhancement of photocatalytic activity of GWx composites was attributed to a direct Z-scheme mechanism in Fig. 4d. Under simultaneous light excitation, the excited electrons in the CB of WO_3 undergo interfacial transfer to $g\text{-C}_3\text{N}_4$ phase, subsequently quenching the photogenerated holes in the VB of $g\text{-C}_3\text{N}_4$ (ca. 1.6 V vs. NHE). The internal electric field at the $g\text{-C}_3\text{N}_4/\text{WO}_3$ interface

provided a driving force for such Z-scheme electron transfer to occur via the direct pathway paved by their host-guest covalent interaction. In this regard, both the internal electric field and the well-defined interface are critical for achieving the spatial separation of charge carriers.

The resulting activity of GWx composites varied according to the content of WO_3 . The best performance of GW40 suggested an appropriate amount of WO_3 was important to achieve the optimal activity of the final composites. Initially, increasing the amount of WO_3 in the range of low weight ratio is favorable for increasing the interfacial covalent interaction between $g\text{-C}_3\text{N}_4$ and WO_3 , thus promoting charge transfer. However, the positive effect of interfacial charge separation could be deteriorated by the intrinsic inactivity of WO_3 for H_2 production. Thus, the overall activity of GWx composites gradually reaches a summit with increasing WO_3 content, while further addition of WO_3 caused an inevitable decrease of photoactivity. Excess amount of WO_3 also increased the possibility of false loading of Pt co-catalyst on its inactive surface and induced inter-particle aggregation, which decreased interfacial contact and lowered photocatalytic performances. Also, it should be noted that the light absorption should remain similar in all the composite/pure samples, due to the similar band gaps of $g\text{-C}_3\text{N}_4$ and WO_3 . Thus, while having the nearly same charge carrier generation rates, the drastically enhanced activities of the $g\text{-C}_3\text{N}_4/\text{WO}_3$ composites should be directly attributed to a much higher conversion efficiency from the photogenerated charge carriers to the final H_2 products. The cycled tests of photocatalytic H_2 production for the champion GW40 sample was shown in Fig. 4e. During the course of 12 h, the GW40 sample consistently demonstrated much higher H_2 generation rates compared with pure $g\text{-C}_3\text{N}_4$. However, a trend of slight decrease was observed for the GW40 sample every time a new cycle was started. Since similar trend was also observed for pure $g\text{-C}_3\text{N}_4$, it might be due to the depletion effect of sacrificial reagents in the suspension system. Besides, the H_2 evolving reaction itself may influence the structural stability and the overall performance of the Z-scheme $g\text{-C}_3\text{N}_4/\text{WO}_3$ junction to some extent, considering that the H_2 gas molecules are expected to bubble from the surface of the flexible $g\text{-C}_3\text{N}_4$ polymer.

To support the above Z-scheme mechanism, theoretical DFT calculations of charge carrier effective mass were performed based

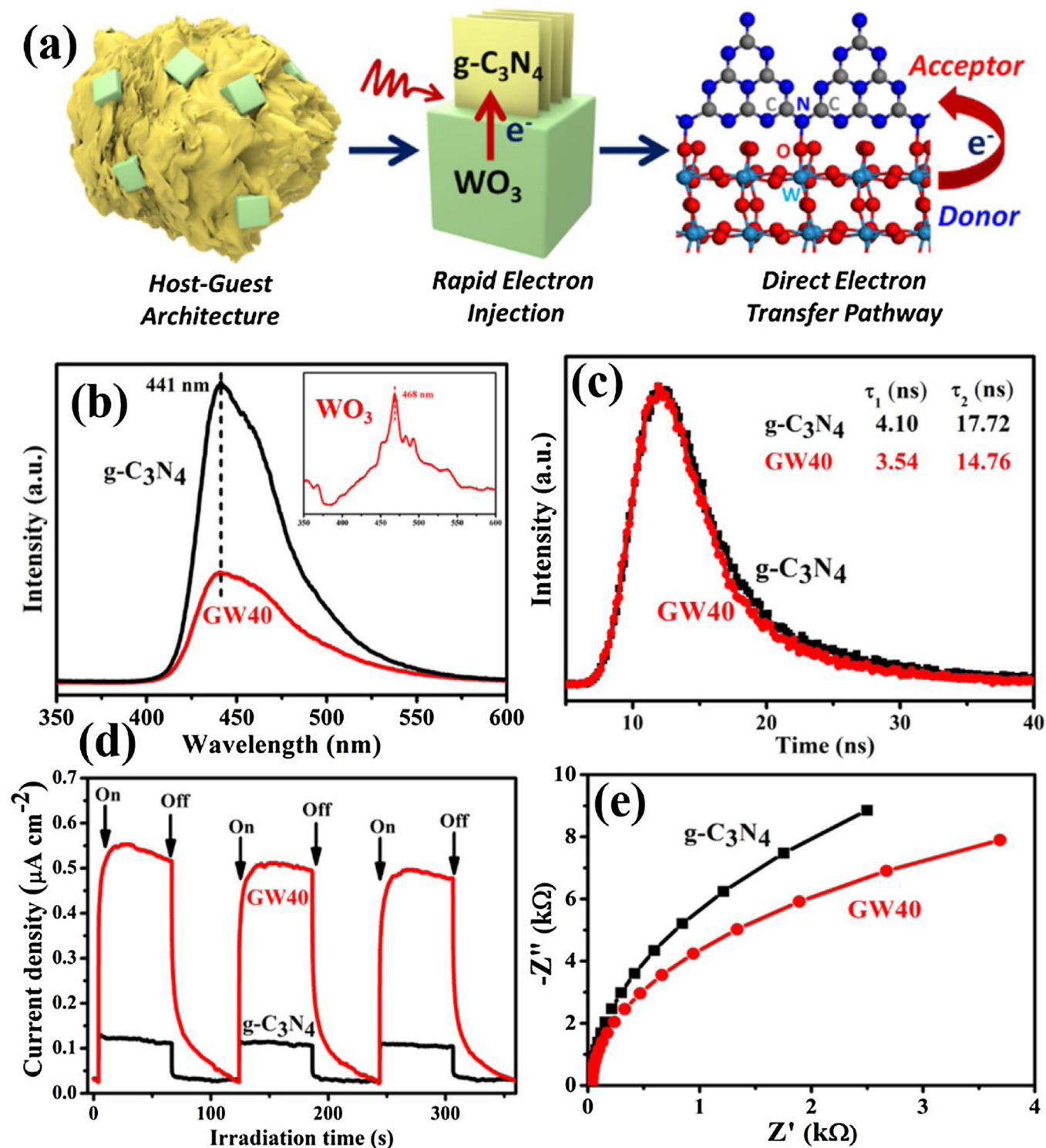


Fig. 6. (a) Schematic illustration of the function mechanism of g-C₃N₄/WO₃ composites at multiple length scales; (b) PL spectra of pure g-C₃N₄, GW40 and pristine WO₃ (inset); (c) time-resolved fluorescence decay profiles of pure g-C₃N₄ and GW40 excited at the wavelength of 320 nm; (d) transient photocurrent response and (e) electrochemical impedance spectra of pure g-C₃N₄ and GW40 in 0.5 M Na₂SO₄ aqueous solution.

on the crystal structures and electronic band structures in Fig. 5 [50,51]. As an anisotropic property, the effective mass of charge carrier needs to be considered separately in different crystal directions. For g-C₃N₄, the calculated results in Table 4 show that its 2D in-plane structure produces much lighter photogenerated electrons (0.53 m_0) and holes (0.72 m_0), as compared with those electrons (1.8 m_0) and holes (71.0 m_0) travelling along its vertical direction

(c axis) [52,53]. The fast mobility of charge carriers within the 2D plane of g-C₃N₄ is attributed to the electron delocalization of π - π conjugation, while the slow charge carrier mobility along its vertical direction was due to the weak electronic coupling between the spatially separated 2D layers. Thus, most charge carriers of g-C₃N₄ should migrate within 2D planes rather than travel through different layers. Recombination factor (R) is defined as the ratio

Table 4

Calculated effective masses of charge carriers of g-C₃N₄ along the designated crystal directions; unit for all the effective masses is m_0 , the electron rest mass.

Direction	G–F	G–Z
m_e^*	0.53	1.8
m_h^*	0.72	71
R	1.3	39

Table 5

Calculated effective masses of charge carriers of monoclinic WO₃ along the designated crystal directions; unit for all the effective masses is m_0 , the electron rest mass.

Direction	G–F	F–Q	Z–Q
m_e^*	0.16	0.17	0.14
m_h^*	0.53	0.49	0.51
R	3.3	2.9	3.6

of the effective mass of hole to electron to evaluate the recombination rate of electron-hole pairs [54,55]. The small value of R for g-C₃N₄ (R = 1.3) suggests that its fast recombination kinetics limits its photocatalytic performance. However, as shown in Table 5, monoclinic WO₃ has not only much lighter charge carriers than those of g-C₃N₄, but also a slower recombination rate of photogenerated electron-hole pairs (R = 2.9–3.6). Compared with g-C₃N₄, the excited electrons of WO₃ demonstrate a higher tendency to migrate from bulk to interface and then transfer into g-C₃N₄. In this regard, the interfacial electron transfer in GWx is more likely to occur from WO₃ to g-C₃N₄, which is consistent with the above direct Z-scheme mechanism.

The function mechanism of the g-C₃N₄/WO₃ composites for enhanced photocatalytic H₂ generation is demonstrated in Fig. 6a. A host-guest architecture in which the small WO₃ nanocuboids were partially intercalated within the large g-C₃N₄ microparticle leads to their simultaneous exposure to light excitation. After charge carrier generation, the higher electron mobility and slower charge recombination in WO₃ directly injected a rapid flow of excited electrons from its CB (donor) into the VB of g-C₃N₄ (acceptor). Besides, the standing morphology of g-C₃N₄ layers on the exposed flat WO₃ facets and their interfacial covalent interaction provided a straight pathway for the electron transfer from WO₃ to g-C₃N₄, driven by the internal electric field at this atomically defined junction. This rapid electron injection quenched the photogenerated holes in g-C₃N₄ and efficiently inhibited its recombination. It should be expected that the accelerated recombination between the electrons in the CB of WO₃ and the holes in the VB of g-C₃N₄ significantly prolongs the lifetime of excited electrons in g-C₃N₄ and thus enables more excited electrons available for H₂ production.

PL spectra were first obtained to evaluate the recombination rate of photogenerated electron-hole pairs (Fig. 6b). The PL spectra of pure g-C₃N₄ and GW40 have similar shapes, exhibiting emission peaks at 441 nm close to the absorption edge of g-C₃N₄. No obvious emission peak from WO₃ is visible for GW40. Thus, the band-band PL phenomenon of g-C₃N₄ is mainly responsible for the PL emission of GW40. The high PL intensity of pure g-C₃N₄ was consistent with its fast recombination rate of photogenerated charge carriers. The much lower PL intensity of GW40 indicates the recombination of charge carriers in bulk g-C₃N₄ is greatly retarded by coupling with WO₃. Time-resolved fluorescence decay profiles of pure g-C₃N₄ and GW40 in Fig. 6c show that both the fast and slow components of the fluorescence lifetime in GW40 ($\tau_1 = 3.54$ ns, $\tau_2 = 17.72$ ns) are shortened as compared with those of pure g-C₃N₄ ($\tau_1 = 4.10$ ns, $\tau_2 = 14.76$ ns). Both the lower PL intensity and the decreased fluorescence lifetime of GW40 strongly prove the presence of charge separation at the g-C₃N₄/WO₃ interface.

Transient photocurrent responses were recorded by typical switch on-off cycles of light irradiation in Fig. 6d. The photocurrent response of GW40 ($0.48 \mu\text{A cm}^{-2}$) is 7 times higher than that of pure g-C₃N₄ ($0.07 \mu\text{A cm}^{-2}$). Under light illumination, the embedded WO₃ nanocuboids promote the charge separation in GWx composites via rapid injection of an electron flow. Both the low value of photocurrent and the quick decay character of pure g-C₃N₄ can be assigned to its fast recombination kinetics. The much higher photocurrent of GW40 suggests that the electron injection from WO₃ to g-C₃N₄ significantly slows down the recombination of charge carriers. Besides, the slower decay kinetics of GW40 at turn-off of light irradiation indicates the prolonged lifetime of excited electrons of g-C₃N₄ phase, consistent with more efficient separation of photogenerated electrons and holes. The electrochemical impedance spectra in Fig. 6e show that the GW40 composite exhibited a reduced radius of Nyquist plot in contrast to that of pure g-C₃N₄. This implies that GW40 composite has a smaller electronic resistance than that of pure g-C₃N₄, due to more effective charge transport and collection. All these above measurements confirm that the g-C₃N₄/WO₃ composite produces more excited electrons with extended lifetime that are available for heterogeneous photocatalytic H₂ production, again supporting the above direct Z-scheme mechanism.

4. Conclusions

In summary, a direct Z-scheme host-guest g-C₃N₄/WO₃ architecture was rationally constructed by partially embedding the guest WO₃ nanocuboids into the host g-C₃N₄. The fabricated g-C₃N₄/WO₃ composite all exhibited dramatically enhanced activities for photocatalytic H₂ production. With the aid of spherical aberration-corrected STEM, the well-defined g-C₃N₄/WO₃ interface was clearly resolved as the 2D g-C₃N₄ layers standing vertically on the flat facets of WO₃ nanocuboids. Unprecedentedly, both the in-plane and interlayer structures of g-C₃N₄ were directly imaged at atomic scale. The internal electric field and the covalent W–O–N–(C)₂ interaction provides the driving force and the direct pathway, respectively, for achieving direct Z-scheme electron transfer from WO₃ to g-C₃N₄ at interface. Under simultaneous light excitation, this atomically defined junction induces a rapid electron injection from WO₃ into g-C₃N₄. In this way, the fast recombination kinetics of g-C₃N₄ is significantly inhibited and the lifetime of its charge carrier lifetime is also prolonged, thus liberating more excited electrons with high reducing power for H₂ production. This work will provide new deep insights into the rational design of g-C₃N₄-based Z-scheme photocatalytic systems for more efficient solar energy utilization.

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